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Potassium/calcium/nickel oxide catalysts for oxidative coupling of methane

Kerry M. Dooley¹ and Julian R.H. Ross²

Department of Chemical Technology, Technical University of Twente, P.O. Box 217, 7500 EA Enschede (Netherlands)

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Abstract

A series of potassium/calcium/nickel oxides were tested for the oxidative coupling of methane (OCM) at 843–943 K and water addition to the feed at 0–65 mol-%. The K/Ni ratios varied from 0.0–0.6 and Ca/Ni from 0.0–11; catalysts with no nickel were also tested. At least 10% water in the feed and temperatures lower than ca. 940 K were necessary to keep nickel-containing catalysts from converting to purely steam reforming/combustion behavior. Catalysts of low (less than 4) Ca/Ni were the most active, with a maximum C₂ selectivity, which increased with temperature, of 37% at 11% C₂ yield (28% water in feed, 933 K). Catalysts of high (4–11) Ca/Ni ratio were less active, with a maximum C₂ selectivity of 32% at 7.1% C₂ yield (43% water in feed, 923 K). Previous claims of higher selectivities for similar catalysts could not be reproduced except at short times on stream, in the absence of substantial carbonate buildup. These transient selectivities were not associated with the nickel-containing phase. At steady state, both C₂ yields and selectivities increased with respect to the water content of the feed, while decreasing with C₁/O₂ ratio. The latter behavior is unusual and may be related to the reduction of higher valent potassium/calcium/nickel oxide. The existence of such material as an active phase for OCM was suggested by the results of X-ray diffraction, differential scanning calorimetry, temperature-programmed reduction, and laser Raman spectroscopic characterizations of fresh and used catalysts.

Keywords: alkali nickel oxide, methane, oxidative coupling.

INTRODUCTION

Group VIII transition metal oxides, and some reducible post-transition metal oxides (especially SnO_x), are materials which have shown promise as pro-

Correspondence to: Prof. K.M. Dooley, Dept. of Chemical Engineering, South Stadium Rd., Louisiana State Univ., Baton Rouge, LA 70803-7303, USA. Tel. (+1-504)3883060, fax. (+1-504)3881476, e-mail DOOLEY@LSUCHE.BITNET.

¹On sabbatical leave from Dept. of Chemical Engineering, Louisiana State Univ., Baton Rouge, LA 70803, USA.

²Current address: Dept. of Industrial Chemistry and Chemical Engineering, Univ. of Limerick, Plassey Park, Limerick, Ireland. Tel. (+353-61)333644, fax. (+353-61)330316, e-mail ROSSJ@UL.IE.

motors for alkali/alkaline earth oxide catalysts used for the oxidative coupling of methane (OCM) [1–8]. The relationship between these materials and alkali molybdate catalysts is at present unclear, but there are X-ray photoelectron spectroscopy (XPS) and other indications of multiple metal oxidation states (e.g., $\text{Ni}^{2+}/\text{Ni}^{3+}$) and participation of lattice oxygen in these catalysts at working conditions [1,5–7]; these are characteristics of alkali molybdate catalysts as well. It has recently been discovered by Heinemann and coworkers [7,8] that inclusion of more than 60% water in the feed to an OCM reactor greatly increases the C_{2+} selectivity of such catalysts at ca. 873 K, by an as yet unknown mechanism [7,8]. This effect of water also parallels experience with the alkali molybdate catalysts, although the selectivity enhancements here are not as pronounced [9,10].

Higher activities (high oxygen conversions at below 1000 K), at only slight penalties in selectivity, have also been observed for Li/MgO catalysts mixed with small amounts of cobalt or tin oxides [11,12]. It has been hypothesized that the presence of a reducible oxidic phase promotes activation of oxygen in a dissociated form suitable for methane activation such as surface O^- [13]. Electron spin resonance (ESR) measurements on $\text{Co}^{2+}/\text{MgO}$ suggest that O^- would not be formed on the surface of transition metal/alkaline earth oxide mixtures in the absence of alkali [14]. In the presence of alkali, $^{16}\text{O}_2/^{18}\text{O}_2$ exchange measurements (for Li/NiO) [2] and XPS measurements on adsorbed oxygen (for $\text{K}^+/\text{Mn}_3\text{O}_4$) [15] at least suggest that O^- may be present, although it is not yet certain that O^- is involved in the selective oxidation.

We have begun a study of alkali/alkaline earth/transition metal oxides as catalysts for OCM. That these catalysts may be useful with water-rich feeds has already been demonstrated by Heinemann and coworkers [7,8]. However, it remains to be seen whether other catalysts of this type require as much water for high selectivity, and whether activities can be increased above the low levels previously observed. These catalysts may also be effective at conventional conditions (higher temperatures, C_1/O_2 ratios > 4 , no water in the feed), but have been only sparingly studied [1,6].

EXPERIMENTAL

CaO/NiO mixed oxides were prepared by coprecipitation of the nitrates at $\text{pH} = 12$, with slight heating, followed by calcination in static air. For some of the catalysts the potassium source was coprecipitated as well; but in most of the preparations KNO_3 was added to the already calcined CaO/NiO by dry mixing, because otherwise retention of potassium was poor. This latter procedure is in accord with that of Pereira et al. [7].

At each Ca/Ni ratio, catalysts of low (K/Ni ca. 0.1) and high (K/Ni ca. 0.5) potassium content were prepared. Final calcination was in-situ prior to kinetics experiments using one of the following procedures:

- (A) 3 cm³/min O₂, 973 K, 40 h
- (B) 3 cm³/min O₂, 1013 K, 40 h
- (C) 3 cm³/min CO₂, 773 K, 4 h; then 2 cm³/min O₂ + 1 cm³/min CO₂, 973 K, 12 h
- (D) same as (C) except 40 h at 973 K

Procedures (C) and (D) were designed to convert KNO₃ to the carbonate before high-temperature calcination, in order to reduce potassium loss by vaporization. The catalysts were pressed and crushed to 0.3–0.6 mm grains prior to these treatments. A K.05/Ca catalyst (no nickel) was prepared following the procedure of Rasko et al. [8]; the final calcination was at 973 K for 18 h in 3 cm³/min air.

Alkali and alkaline earth analyses were carried out using atomic absorption spectroscopy (AAS), while transition metal concentrations were determined by X-ray fluorescence (XRF). The catalysts are designated in terms of the atomic ratios of potassium/calcium/nickel. The initial Ca/Ni ratio in all cases decreased somewhat upon calcination due to absorption of CaO by the combustion boats. The ratios given here were measured after the final calcination, but prior to OCM reaction.

X-ray diffraction (XRD) measurements were made on a Philips P.W. 1710 diffractometer using Cu K α radiation at 1.5418 Å. Differential scanning calorimetry (DSC) measurements were made using a Stanton Redcroft PL 700 DSC using oxygen, nitrogen, air, or a 50% H₂/50% N₂ mixture as the carrier gas, at 30–40 cm³/min. Thermogravimetric analyses (TGA) with temperature programs and gas flow-rates simulating final in-situ calcinations were performed using a DuPont 951 TGA. For laser Raman spectroscopy, the 514.5 nm line of an Ar⁺ laser at 20 mW was used for excitation. A triple monochromator (Spex 1877) was used with 100 s accumulation of signal. Samples were powdered, pressed, and mounted on glass slides.

The kinetics measurements were performed in a conventional microreactor flow system with on-line gas chromatography (GC) analysis. The reactor was 1.25 cm I.D. with a 10 cm bed length, with the catalyst held between 0.3–0.6 mm quartz beads. The C₁/O₂ ratio was 2.3–2.7 unless otherwise noted, and the methane weight hourly space velocity (WHSV) was 0.40 \pm 0.01 h⁻¹ with total flow-rates in the range 30–50 cm³/min. Methane, oxygen, and helium (if used) were metered and mixed using Brooks 5850 mass flow controllers. When water was added to the feed, it was supplied from a saturator which was controlled by a constant (\pm 1 K) temperature bath.

RESULTS

Catalyst activity measurements

Blank runs (quartz beads only) at 16 and 27% water in the feed were performed using a feed of molar ratio CH₄/C₂H₆/O₂ = 2/2/1. This feed simulated

a normal feed that has undergone 50% oxygen conversion to produce ethane selectively. The purpose of this experiment was to determine how much of the ethane produced by the catalyst under best-case conditions might have been decomposed to CO_x in gas-phase reactions. This is a more stringent test of the effects of post-reactor dead volume than a blank experiment with only a $\text{CH}_4/\text{O}_2/\text{H}_2\text{O}$ feed. At the highest temperature studied, 936 K, the total carbon conversions found using this mixed feed were 18% (for 16% water in the feed) and 17% (27% water), with CO_x selectivities of 28% (16% water) and 27% (27% water), respectively; the oxygen was completely converted. From these numbers it can be calculated that at our normal reactor conditions only at most ca. 5% of the total carbon could react to CO_x by reactions not occurring on the catalysts. For a typical methane conversion of 30%, this corresponds to an achievable C_{2+} selectivity of ca. 80% at worst case conditions.

Except at short times-on-stream, the carbon balances for all data reported here were within 10%, most within 5%; the hydrogen balances were within 5%. The oxygen conversions for the nickel-containing catalysts were near 100% at temperatures higher than 903 K; when the Ca/Ni ratio was low, they were near 100% except below 873 K. The oxygen conversions for the K.05/Ca catalyst were typically 0–50% except when the feed C_1/O_2 ratio was high.

The effects of the four different calcination procedures on the performance of a single representative catalyst (K.1/Ca1.2/Ni) was first examined. Fig. 1 shows the results of reaction experiments at different temperatures, including a repeat measurement after longer term (> 12 h) use. In this and all subsequent figures, such a repeat measurement is denoted by a line connecting the repeat datum to the datum at highest temperature; in other words, the exact temperature progression used in the experiment is shown.

It is evident from Fig. 1 that calcination in the absence of carbon dioxide resulted in a catalyst with poorer stability. Calcination in the presence of car-

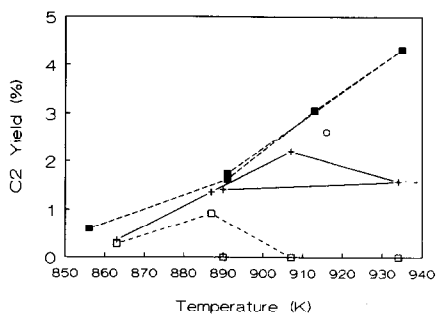


Fig. 1. Effect of calcination conditions, K.1/Ca1.2/Ni catalyst, C_1/O_2 ca. 2.5. (+) (A) 973 K, 40 h, $3 \text{ cm}^3/\text{min O}_2$; (\square) (B) same as A but 1013 K; (\blacksquare) (C) 773 K, 4 h, $3 \text{ cm}^3/\text{min CO}_2$, then 973 K, 12 h, $2 \text{ cm}^3/\text{min O}_2 + 1 \text{ cm}^3/\text{min CO}_2$; (\circ) (D) same as C except 40 h at 973 K. + and \square , 22–33% water in feed; \blacksquare and \circ , 14% water.

bon dioxide gave higher yields at the higher temperatures, although there was loss of selectivity and potassium at long times-on-stream. The material used in Fig. 1 (treatment C) lost 27% of its potassium and 20% of its total selectivity to C_2 products in 40 h time-on-stream at 935 K. All subsequent results for nickel-containing catalysts were obtained using procedure C.

The effect of the water content of the feed on the performance of nickel-containing catalysts is shown in Fig. 2 for a K.1/Ca.8/Ni catalyst. It is evident that increasing the concentration of water in the feed increased the C_2 yield. This effect was nonlinear; the largest increase in yield occurred when the water content was increased from 0 to 25%, with smaller increases in yield observed upon further increases in water content. Total activity also depended on water content; in a related experiment, a step change in feed composition from 65 to 30% water at 873 K caused a decrease in methane conversion from 32 to 19% and in C_2 selectivity from 20 to 13%.

Any nickel-containing catalyst operated in the absence of water in the feed ultimately displayed only reforming, combustion, and coking activity, with reforming to carbon monoxide and hydrogen being the dominant reaction. At these conditions there was rapid carbon accumulation at short times-on-stream. The conversion from an OCM to a reforming catalyst was rapid (less than 3 h) and was accompanied by large increases in C_1 conversion, CO/CO₂ ratio, and hydrogen production. The presence of 10% water in the feed was found adequate to prevent this transformation.

A catalyst presaturated with water for a long period could still catalyze OCM for several hours, even after helium was substituted for water. A catalyst's behavior subsequent to such a step-change is shown in Fig. 3. The yields shown are still typical of a catalyst with ca. 25% water in the feed (compare to Fig. 2).

The normal C_1/O_2 ratio used in OCM reaction experiments was about 2.5. At these conditions the maximum steady-state C_2 selectivity for nickel-containing catalysts was about 40%. This maximum was obtained with potassium-

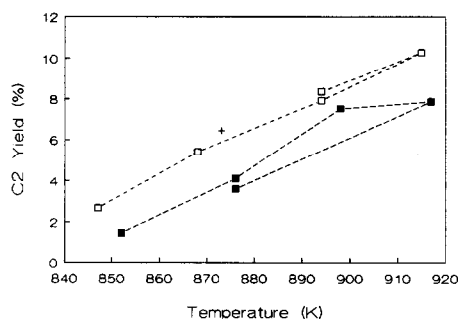


Fig. 2. Effect of variable water content, K.1/Ca.8/Ni catalyst, C_1/O_2 ca. 2.5; (+) 65 mol-% water in feed, (□) 46%, (■) 25%.

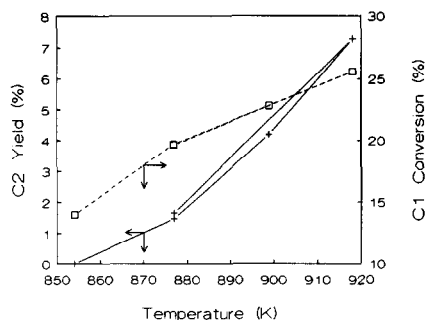


Fig. 3. Behavior of K.1/Ca.8/Ni catalyst after step change in feed content from 25% H₂O to 25% He, C₁/O₂ ca. 2.5; (+) percent C₂ yield, (□) percent C₁ conversion. The water pretreatment was for 24 h at 873 K. Each data point corresponds to ca. 2 h time-on-stream.

TABLE 1

Detailed results for most selective catalysts

K/Ca	0.05	0.05	0.17	0.44
Ca/Ni	—	—	0.75	1.32
K/Ni	—	—	0.13	0.58
Temperature (K)	935	935	915	934
C ₁ /O ₂	53	3.3	2.7	2.3
Water (%)	38	34	46	28
WHSV ^a	0.40	0.40	0.40	0.39
TO ^b	> 4	> 4	> 1.6	> 3.5
STY ^c	0.012	0.018	0.042	0.045
HC Sel. ^d (%)	67	37	39	37
HC Sel. (%)	55	31	25	0 ^e
C ₁ Conv. (%)	4.5	13.6	26.6	30.0

n.r. not reported

^a Methane WHSV; the actual reactor residence time is about 1 s.

^b Number of turnovers based on average conversion, grams methane converted per gram catalyst.

^c Space-time yield, grams methane converted to higher hydrocarbons per gram catalyst per hour.

^d Highest selectivity reported; lowest selectivity in next row; in this work, only C₂ hydrocarbons were analyzed.

^e Converts to reforming catalyst (CO+H₂ products) after several hours on-stream at this temperature.

containing catalysts of low (less than 4) Ca/Ni at complete oxygen conversion, and at 903–933 K. Claims of much higher selectivities have been made for similar catalysts by Heinemann and coworkers at similar conditions [7,8]. Table 1 gives detailed, averaged results for our most selective catalysts. Compared to results of Heinemann and coworkers, our space-time yields (production rates of higher hydrocarbons) were higher, and our catalysts were kept on stream for relatively longer periods, because we employed a six times higher

space velocity. At short times-on-stream, with catalysts of Ca/Ni ratio > 2 , we also observed high selectivities at lower than 873 K (similar to results in refs. 7 and 8). However, these selectivities did not last for a complete turnover based on the weight of catalyst used. These transient, initial selectivities are reported in Table 2.

The effects of C_1/O_2 ratio on the performance of K.6/Ca1.3/Ni are shown in Fig. 4. The methane partial pressure for these experiments was kept constant by the addition of helium at the higher C_1/O_2 ratios. It is noteworthy that for the nickel-containing catalysts both C_2 yields and C_2 selectivities increased as the C_1/O_2 ratio decreased. This behavior is in contrast to most OCM catalysts, whose C_2 selectivities decrease monotonically while yields either decrease or go through a maximum (e.g., Li/MgO [16], Sm_2O_3 [17], PbO/MgO [18], Mn/ $Na_4P_2O_7/SiO_2$ [19]).

The potassium content of the nickel catalysts appeared to affect C_2 production only slightly. This is evident from Fig. 5 upon comparing the upper two

TABLE 2

Initial selectivities for catalysts of high Ca/Ni
 $C_1/O_2 = 2.3-2.7$

Catalyst	Temperature (K)	C Bal. ^a (%)	H ₂ O (%)	S_{C_2} (%)	C_1 Conv. (%)
K.05/Ca5/Ni	863	58	35	54	3.6
K.05/Ca5/Ni ^b	863	102	35	0.0	3.7
K.6/Ca11/Ni	852	85	41	72	3.6
K.6/Ca11/Ni ^b	852	99	43	0	4.5
K.6/Ca11/Ni ^c	852	103	44	30	0.84

^a $100 \times (\text{carbon out}) / (\text{carbon in})$.

^b After 12 h time-on-stream.

^c After 12 h time-on-stream and extra 24 h oxygen treatment at 700°C.

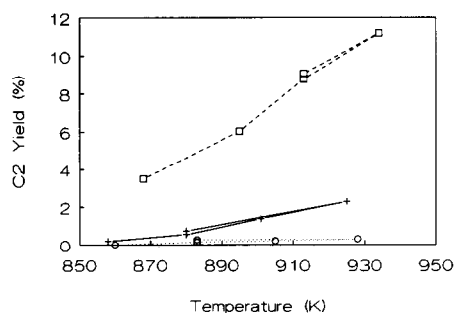


Fig. 4. Effect of C_1/O_2 ratio, K.6/Ca1.3/Ni catalyst, 24-29% water in feed; (□) $C_1/O_2 = 2.3$, (+) 4.6, (○) 44.

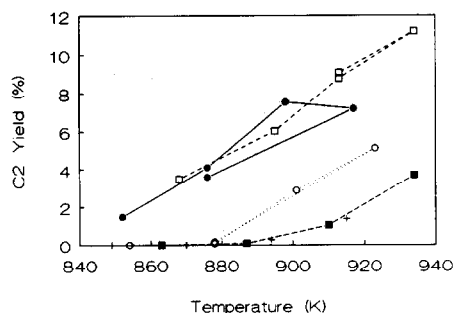


Fig. 5. C₂ yield for five different catalyst compositions at 24–35% water in the feed, C₁/O₂ ca. 2.5; (●) K.1/Ca.8/Ni, (□) K.6/Ca1.3/Ni, (○) K.2/Ca10/Ni, (■) K.05/Ca5/Ni, (+) K.05/Ca.

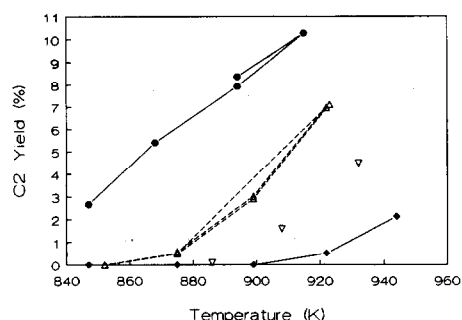


Fig. 6. C₂ yield for four different catalyst compositions at 41–47% water in the feed, C₁/O₂ ca. 2.5; (●) K.1/Ca.8/Ni, (Δ) K.6/Ca11/Ni, (▽) K1.2/Ca4/Ni, (◆) K1.5/Ni.

curves describing the performance of two catalysts of similar Ca/Ni ratio. It should be noted that the K.6/Ca1.3/Ni catalyst became less selective when kept for several hours at temperatures higher than 930 K, so even at high temperature the differences between this catalyst and K.1/Ca.8/Ni may not be significant.

The more important determinant of C₂ yield was Ca/Ni ratio, as seen upon examination of both Figs. 5 and 6. In both figures it is evident that materials of low (less than 4) Ca/Ni ratio were superior, and that materials either without nickel (the K.05/Ca results in Fig. 5) or calcium (the K1.5/Ni results in Fig. 6) were poor catalysts. The behavior of potassium/calcium/nickel materials of high Ca/Ni ratio fell between these two groups. The maximum selectivity of the high Ca/Ni catalysts was only 32%.

At high C₁/O₂ ratios the yield improved for the K.05/Ca catalyst, as shown in Fig. 7. Note that this behavior of increasing yield with respect to C₁/O₂ ratio (at roughly constant methane partial pressure) is exactly opposite that found for the nickel-containing catalysts. A maximum selectivity of 67% was found for this catalyst, at its highest temperature and oxygen conversion. Even at

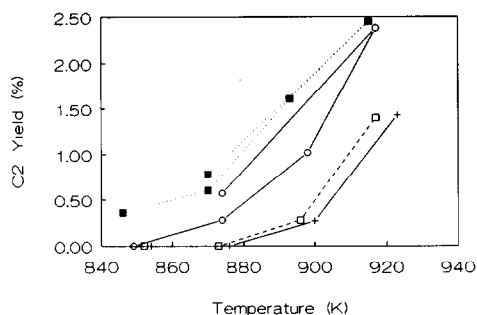


Fig. 7. Effect of C_1/O_2 ratio and water content of the feed, K.05/Ca catalyst; (+) $C_1/O_2 = 3.3$, 36% water; (□) 3.3, 27%; (○) 53, 22%; (■) 52, 38%.

TABLE 3

Bulk phases identified by XRD

Catalyst	Major phases	Minor phases
K.05/Ca, fresh	CaO, Ca(OH) ₂	CaCO ₃ , tr. KO ₂
K.05/Ca, used	Ca(OH) ₂	Ca(CO) ₃
K.2/Ca10/Ni, fresh	CaCO ₃ , CaO	Ca(OH) ₂ , NiO
K.2/Ca10/Ni, used	CaCO ₃	Ca(OH) ₂ , NiO, CaO
K.05/Ca5/Ni, fresh	CaO, NiO	Ca(OH) ₂ , CaCO ₃ , tr. NiOOH
K.5/Ca4/Ni, fresh	CaO, NiO	Ca(CO ₃), tr. NiOOH
K.5/Ca4/Ni, used	CaO, NiO, Ca(CO ₃)	Ca(OH) ₂ , tr. NiOOH
K.1/Ca.8/Ni, fresh	NiO, CaO, Ca(OH) ₂	CaCO ₃ , tr. NiOOH
K.1/Ca.8/Ni, used	NiO, CaCO ₃	CaO ₂ , tr. NiOOH, tr. K ₂ Ca(CO ₃) ₂
K.6/Ca1.3/Ni, fresh	NiO, CaO, Ca(CO) ₃	NiOOH, CaO ₂ , K ₂ CaCO ₃
K.6/Ca1.3/Ni, used	NiO, CaCO ₃ , Ca(OH) ₂	CaO, K ₂ Ca(CO ₃) ₂ , CaO ₂

Tr. = Trace amount.

$C_1/O_2 > 50$, oxygen conversions were less than 100% until > 910 K. However, water was reacted and hydrogen formed. For example, with 38% water in the feed, 2–7% of the water was depleted, in contrast with the nickel-containing catalysts which always produced water.

Catalyst characterization

The bulk phases in the catalysts were determined by XRD. In Table 3, “fresh” catalyst denotes a calcined material not yet used in a kinetics experiment. A large increase in carbonate content was evident when used catalysts were compared to fresh ones by either XRD or TGA. Also, a new minor phase either appeared or grew in used materials of low Ca/Ni; this phase was identified as $K_2Ca(CO_3)_2$. No other potassium-containing phase could be identified by XRD in materials containing nickel.

Some fresh and used catalysts were further examined by DSC using either air, 50% H_2 /50% N_2 , or carbon dioxide (to 773 K) followed by oxygen (to 993 K) carrier gases. Already calcined materials were stable in air up to 1073 K when examined by DSC. Two samples (K.01/Ca.2/Ni and K.1/Ca1.7/Ni) were tested, and no transitions noted unless carbon dioxide had been used in the calcinations. When treated with H_2/N_2 , however, several endotherms were found as shown in Fig. 8 (endothermic transitions plotted as negative) for some used catalysts and an NiO (Baker, reagent) standard. Only the highest temperature, broad endotherm (which was incomplete even at 1073 K) cannot be fully attributed to carbonate decomposition or water loss; the lower-temperature endotherms were also found for materials which were temperature-programmed using carbon dioxide, followed by oxygen.

The final in-situ calcinations of materials with different potassium contents were also performed in both the DSC and the TGA. The purpose here was to observe the decomposition of the KNO_3 and the possible incorporation of potassium into a nickel oxide. Some of these results are shown in Fig. 9; results for a material with no nickel (K.05/Ca) and no potassium (Ca4/Ni) are shown for comparison purposes. The primary low-temperature endotherm at 630–710 K can be attributed to the decomposition of KNO_3 , because this endotherm is absent from Ca4/Ni and this temperature range spans the reported decomposition temperature of the pure compound, 673 K [20]. The weight loss in nitrogen was 5.7% vs. 5.6% calculated for decomposition to K_2O . For materials containing both potassium and nickel there is a broad exotherm noticeable in the 720–930 K range, especially for samples calcined in oxygen. The TGA results confirmed that this exotherm was associated with small (less than 1%) weight gains; however, the weight gains were much larger when O_2/CO_2 mixtures were used.

These results confirmed that KNO_3 was decomposed at the calcination temperatures, even in nitrogen atmosphere. We hypothesize that the exotherm

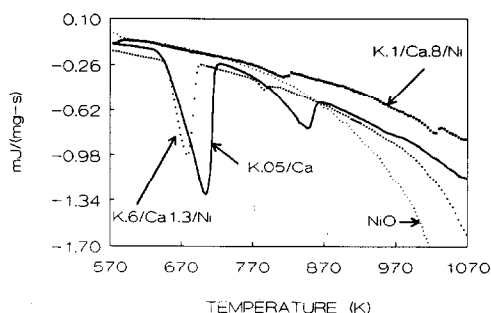


Fig. 8. Example temperature-programmed reduction spectra of used catalysts in a DSC; solid curve: K.05/Ca, (\square) K.1/Ca.8/Ni, (+) K.6/Ca1.3/Ni; dotted curve: NiO. Carrier gas is 50% H_2 /50% N_2 at 30 cm^3/min . Endothermic transitions plotted as negative.

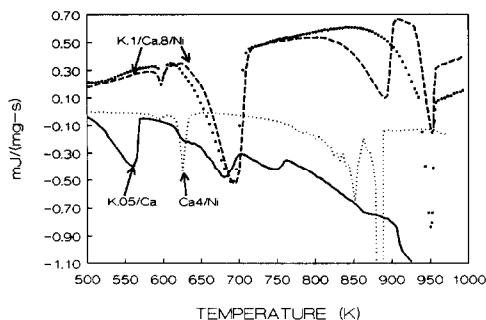


Fig. 9. DSC of calcinations with oxygen of potassium/calcium/nickel oxides, all prepared using KNO_3 ; (\square) K.1/Ca.8/Ni; dashed curve: same but nitrogen carrier gas; dotted curve: Ca4/Ni; solid curve: K.05/Ca. Carrier gas flow is $30 \text{ cm}^3/\text{min}$. Endothermic transitions plotted as negative.

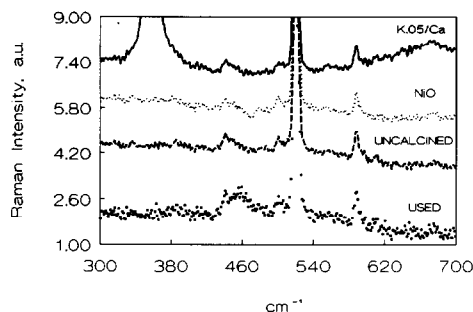


Fig. 10. Raman spectra of K.1/Ca.8/Ni and comparison standards; (\square) used catalyst; dashed curve: uncalcined catalyst; dotted curve: NiO; solid curve: K.05/Ca, used.

subsequent to this decomposition represents the dissolution of liberated K_2O in the NiO_x . Although this exothermic transformation was complicated by carbonation in the presence of carbon dioxide at temperatures lower than 770 K and decarbonation at higher temperatures, we note in support of our hypothesis that the Ca4/Ni sample showed no exotherm at all (Fig. 9).

Raman spectra in the range $300\text{--}700 \text{ cm}^{-1}$ for the K.1/Ca.8/Ni catalyst were compared to spectra of NiO and K.05/Ca as shown in Fig. 10. The bands centered at 441, 520 and 587 cm^{-1} were common to all samples and can therefore be attributed to sample fluorescence. However, two important features were noted: (1) the strong carbonate bands at 357 and 675 cm^{-1} did not appear in materials of low Ca/Ni; (2) in calcined and used nickel-containing catalysts there was noticeable growth of a band centered at $460\text{--}470 \text{ cm}^{-1}$.

DISCUSSION

The low (less than 4) Ca/Ni catalysts exhibited low-temperature activity, with yields of 5–8% possible even at 890 K; such yields would require about

970 K using a MgO-based OCM catalyst such as Li/Sn/MgO [12]. However, the selectivities obtained here were low, about 40% maximum vs. 80% maximum for Li/Sn/MgO, and large amounts of catalyst were required.

Results in Table 2 suggest that the high C₂ selectivities obtained using catalysts of high Ca/Ni at low temperature were transient. Loss of low-temperature activity coincided with improvement in the carbon balance, suggesting bulk carbonate formation. This was confirmed by XRD (Table 3) and Raman results showing growth of a bulk Ca(CO)₃ phase upon use. It is noteworthy that C₂ production at these conditions ceased completely; therefore, these very active sites for C₂ production were poisoned.

The results of the calcination experiments performed in the DSC (Fig. 9) support the above interpretation. Treatment with oxygen or nitrogen resulted in an endotherm at higher than 870 K that is attributed to carbonate decomposition by analogy with pure calcite [21–23]. Furthermore, the transient C₂ selectivities at lower than 873 K were also observed with K.05/Ca, but not with nickel-containing catalysts of low Ca/Ni. Putting these observations together, we conclude that the very active sites for transient C₂ formation are associated with carbonate-free potassium/calcium oxide. For materials of low Ca/Ni, these sites were not present, because the high C₂ selectivities were not observed even when carbon dioxide was not used in the final calcination (e.g., procedures A and B of Fig. 1).

For K.05/Ca also, no C₂ products were found at lower than 873 K after a satisfactory carbon balance was achieved. However, this catalyst could produce C₂'s at high selectivity and at space-time yields larger than those previously reported [8] when the temperature was increased. Increasing the C₁/O₂ ratio had these same effects.

Certain aspects of the structure of the selective phase of the potassium/calcium/nickel oxides (low Ca/Ni) can be inferred from the results. Nickel is important in generating a more active catalyst (Fig. 5), as is calcium (Fig. 6). There was no evidence of bulk potassium oxides, hydroxides, or carbonates by XRD, even for K.6/Ca1.3/Ni where potassium made up 10.5 wt.-% of the calcined catalyst. Therefore, all of the potassium, except for the seemingly small amounts in K₂Ca(CO₃)₂, was dissolved in either a primarily nickel oxide or a primarily CaO/CaCO₃ phase. We note that alkalis can be readily included in NiO [24] and NiOOH [25,26] in oxidizing atmosphere at low temperature, and bulk alkali nickel oxides can be formed [27,28].

The addition of small amounts of potassium to nickel reforming catalysts reduces turnover frequencies for methane steam reforming by two orders of magnitude at 773 K [29], in agreement with our finding of no obvious steam reforming with the nickel-containing catalysts at normal reaction conditions. With these materials we observed: (a) minimal hydrogen production; (b) low CO/CO₂ ratios; (c) no net water consumption; (d) catalyst stability at water/carbon ratios as low as 0.14, while the minimum water/carbon ratios to prevent

carbon deposition in methane steam reforming are ca. 0.3–0.4 [30]. However, conditions (a) and (c) were not fulfilled for K.05/Ca; these differences and the differing behavior with respect to C_1/O_2 ratio again suggest that the nickel-containing catalysts are fundamentally different. The onset of noticeable steam reforming activity for the nickel-containing catalysts, at higher than 930 K, coincided with complete loss of C_2 yield.

The above discussion ignores the CaO/CaCO₃, however. Our data are insufficient to explain fully the role of calcium in these catalysts. At the synthesis conditions used here a single phase alkaline earth nickel oxide could not be formed; only solid solutions of Ni/CaO and Ca/NiO with less than 2 wt.-% solubility of the guest cation in either phase [31] would be possible, if potassium did not greatly affect these solubilities. As CaO by itself is a poor catalyst at these conditions [8], it is likely that potassium improves the solubility of nickel in CaO or calcium in NiO_x, or both.

The evidence that some Ca²⁺ must be associated with a potassium nickel oxide phase can be summarized as follows:

- (1) the poor catalytic performance of K1.5/Ni (Fig. 6);
- (2) the absence of (transient) high selectivities at lower than 873 K for catalysts of low Ca/Ni;
- (3) the temperature-programmed reduction (TPR) results (Fig. 8) showing that calcium-containing catalysts are stable to reduction of NiO to nickel; these results are analogous to the known effects of MgO on the reducibility of NiO [32,33];
- (4) the Raman spectrum of used K.1/Ca.8/Ni (Fig. 10) showing the relative absence of the carbonate buildup so evident for materials of high Ca/Ni.

For both our potassium/calcium/nickel catalysts and those of Pereira *et al.* [7], C_2^+ selectivity decreased at temperatures higher than ca. 930 K, but not irreversibly unless the catalysts remained at high temperature for more than a few hours (e.g., see the repeat measurements in Figs. 1, 2, and 5). Such behavior suggests an active phase or surface based on a hydroxide or adsorbed water; alkali inclusion does promote nickel oxyhydroxide formation [24,25,34]. Wet A_{0.2}NiO₂ alkali nickelates are indistinguishable by XRD from the material denoted γ -NiOOH, some of whose major reflections appear in some of the nickel-containing catalysts, although the XRD results were not conclusive on this point. Because nickel oxyhydroxides are reduced to NiO in strongly reducing atmospheres, we might expect an increasing C_1/O_2 ratio to affect adversely the nickel-containing catalysts, as was the case here (Fig. 4). The completely opposite behavior of the K.05/Ca catalyst (Fig. 7) suggests that the behavior observed in Fig. 4 must be associated with a nickel-containing phase.

The Raman band growth in the 470–480 cm⁻¹ region (Fig. 10) is consistent with our hypothesis on the active surface. The Raman spectrum of pure NiO

features bands at 460 and 500 cm^{-1} of similar intensity [35]. These bands were present both for the uncalcined catalyst and for the NiO standard. The formation of alkali-containing nickel oxyhydroxides by the oxidation of $\text{Ni}(\text{OH})_2$ electrodes in alkaline medium results in the appearance of a band at 470–480 cm^{-1} , attributed to higher valent nickel oxyhydroxides [36,37]. The band at 502 cm^{-1} grew imperceptibly upon calcination and use, so the growth of intensity at 470–480 cm^{-1} was not merely a result of large differences in the fraction of total NiO_x .

Extensive reduction to bulk nickel can probably be excluded as a cause of deactivation on the basis of the TPR results (Fig. 8). The magnitudes of the high-temperature (incomplete at 1073 K) endotherm for most of the used nickel-containing catalysts were actually smaller than the comparable endotherm of K.05/Ca. This was also true of unused but calcined samples. The comparable magnitude for K.6/Ca1.3/Ni was slightly larger, but this is to be expected on the basis of its higher potassium content, because potassium loss also took place at temperatures higher than 930 K.

CONCLUSIONS

(1) The nickel-containing catalysts of low Ca/Ni ratio (less than 4) are active for OCM in the presence of at least 10% water in the feed, but selectivities are low (maximum ca. 40%). Both activities and selectivities increase as the water content of the feed increases. Such catalysts contain an active potassium/calcium/nickel oxide which is hydrated and probably contains some $\text{Ni}^{3+}/\text{Ni}^{4+}$. The observed loss of selectivity as C_1/O_2 is increased may be related to reduction of this higher valent nickel to NiO.

(2) A catalyst with no nickel is far less active but capable of much higher selectivity (maximum 67%), which increases with respect to C_1/O_2 ratio.

(3) Catalysts of high (higher than 4) Ca/Ni ratio are also less active, and exhibit lower selectivities as well.

(4) Calcination of potassium/calcium/nickel oxides in a CO_2/O_2 mixture gives a catalyst with better high-temperature stability, although loss of C_2 selectivity and potassium still takes place upon prolonged use at higher than 930 K.

(5) High C_2 selectivities at lower than 873 K are apparently associated with carbonate-free potassium/calcium oxides. The active sites associated with this behavior are poisoned by carbonate buildup.

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